Unveiling the (De)coupling of magnetostructural transition nature in magnetocaloric $R_5Si_2Ge_2$ (R = Tb, Gd) materials

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We present a detailed study on the magnetization under high magnetic fields of $Tb_5Si_2Ge_2$ and $Gd_5Si_2Ge_2$ compounds. From the Arrott plot construction (A. Arrott, Phys. Rev. **108**, 1394 (1957)), we were able to estimate the T_C of each structure (*M* and *O(I)*) experimentally and found that the T_C of the *O(I)* phase can be directly obtained by extrapolating the T_C curve of this phase in the respective phase diagram. Using a physical model based on free energy considerations, one explains the (de)coupling of the magnetic and structural transitions in $R_5(Si_xGe_{1-x})_4$ (R = Tb, Gd) compounds. © *2011 American Institute of Physics*. [doi:10.1063/1.3640213]

There is a great deal of interest in using the magnetocaloric effect (MCE) as an alternative technology for refrigeration both at room and cryogenic temperatures, since the magnetic refrigeration (MR) is an environmentally friendly cooling technology.[1] Several materials are being envisaged for MR systems. In particular, we stress the $R_5(Si_xGe_{1-x})_4$ compounds with R = Gd and Tb, since they present the widest temperature range and the highest absolute value of ΔS_M.[2] This extraordinary effect essentially arises from the spontaneous 1st-order structural transition from an orthorhombic [*O(I)*] to a monoclinic (*M*) phase (de)coupled to a magnetic transition from a ferromagnetic (FM) to a paramagnetic (PM) phase[3] that can be easily triggered by an applied magnetic field and/or an applied hydrostatic pressure.[4,5] There are scarce studies on the nature of these magnetostructural transitions (MST). In particular, we highlight the theoretical works performed by Paudyal *et al.*[6,7] for $Gd_5(Si_x\ Ge_{1-x})_4$ system. They estimated that *M* and *O(I)* structures present similar internal free energies but with different critical order temperatures and that the structural transition could be explained by considering only the magnetic entropy variation and the free energies at T = 0 K. Herein, we present the effect of high magnetic fields on the magnetization of $Tb_5Si_2Ge_2$ and $Gd_5Si_2Ge_2$ compounds and their ability to induce a MST in the PM phase. Both compounds exhibit a [*M*, PM] phase at room temperature.[4,8,9] On cooling, the Gd compound displays only a 1st-order magneto-structural transition, changing from the [*M*, PM] to the [*O(I)*, FM] phase at $T_S \sim 276$ K.[10] The Tb compound presents two distinct phase transitions: one of 2nd-order and simply magnetic [*M*, PM]→[*M*, FM], which occurs at $T_C = 112$ K followed by a 1st-order structural change of the [*M*, FM]→[*O(I)*, FM] type, which occurs at a lower temperature $T_S \sim 95$ K.[9] In this way, the study of $Tb_5Si_2Ge_2$ can help to unveil the interplay between the spin and lattice components. These materials were prepared following the synthesis referred in Ref. 11 and the isothermal magnetization curves [M(H)] measurements were performed using an extraction magnetometer in a Bitter magnet, HFML (Nijmegen, NL). *ab-initio* calculations were performed using the Wien2K code[13] *via* the augmented plane wave method with local orbitals (APW+lo) approach. Figures 1(a) and 1(b) display the M(H) for $Tb_5Si_2Ge_2$ and $Gd_5Si_2Ge_2$, under H up to 31 T and in the temperature range of 77–340 K. A step-like jump is observed in the experimental M(H) curves, in an intermediate temperature range (98–145 K for Tb and 280–340 K for Gd), from a low initial magnetization state (LM) to a high magnetization state (HM). The change of this magnetization state occurs at a critical magnetic field (H_C) that depends on the path of magnetic field (increase or decrease of magnitude). In order to obtain knowledge about the nature of the magnetic phase transitions, we used the Arrot plot representation since it is a simple but effective method to obtain such information (Figs. 1(c) and 1(d))[14] (see supplementary material[18]). Analyzing the H/M vs M^2 plot for the $Tb_5Si_2Ge_2$ compound [Fig. 1(c)], one observes that the curves in the shadowed region (T < 166 K) exhibit two different linear regimes. This indicates that, for this temperature range, the magnetic field is sufficient to induce the [*M*, PM]→[*O(I)*, FM] transition presenting considerably different susceptibilities [inset of Fig. 1(c)) and see supplementary material[18]]. The spontaneous magnetization M (T, H = 0) can be estimated through a linear extrapolation of the high magnetization field data (see supplementary material[18]); the results obtained are depicted in Fig. 2(a). Notice that this is the spontaneous magnetization of the HM state, i.e., of the *O(I)*

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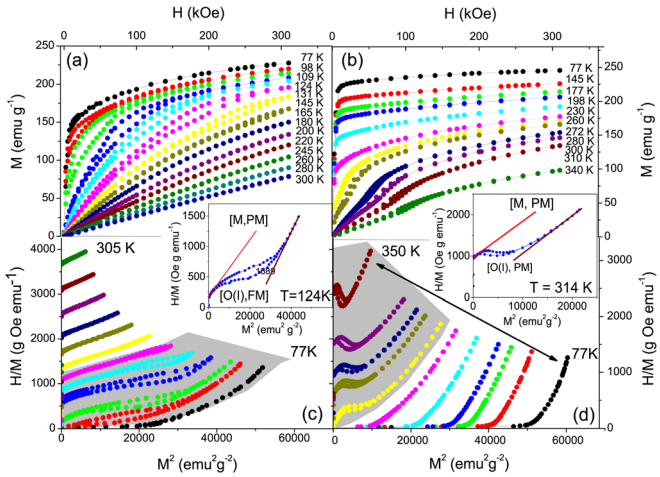

FIG. 1. (Color online) M(H) isothermal magnetization of: (a) $Tb_5Si_2Ge_2$ in the temperature range of 77–300 K and (b) $Gd_5Si_2Ge_2$ in the temperature range of 77–340 K, for applied fields H up to 31 T. Arrott plots for: (c) $Tb_5Si_2Ge_2$ (Inset: T = 124 K) and (d) $Gd_5Si_2Ge_2$ (Inset: T = 314 K).

structure. The PM susceptibility of the *M* phase can be directly determined from the low field isothermal curves (T > 112 K). The χ^{-1} is also displayed in Fig. 2(a) (dot points). From these results, we were able to estimate experimentally the critical temperatures of the *O(I)* ($T_C^{O(I)} \sim 200 \pm 2$ K) and *M* structures ($T_C^M \sim 112 \pm 3$ K), with the former being coincident with order temperature of $Tb_5Si_2Ge_2$.[9] In the Gd case, the same analysis was performed (see supplementary material[18]), leading to $T_C^{O(I)} \sim 308 \pm 2$ K and $T_C^M \sim 251 \pm 5$ K. These experimental results are in fair accordance with the values used by Paudyal *et al.* on their theoretical calculations ($T_C^{O(I)} \sim 305$ K and $T_C^M \sim 208$ K).[6,7] Nevertheless, the explanation for the obtained $T_C^M \sim 251$ K from the PM susceptibility relies only on four available M(H) isotherms, probably justifying the higher value obtained. Additionally, the presence of a small amount of *O(I)* phase (commonly observed for this particular composition) in the Gd sample can also contribute to the experimental value of T_C^M. One immediately recognizes that $Tb_5Si_2Ge_2$ orders ferromagnetically considerably above the *M*→*O(I)* transition ($T_S \sim 95$ K), i.e., this system has $T_S < T_C^M$, whereas for the Gd compound, one has $T_S > T_C^M$. In Fig. 2(b), the linear temperature dependence of H_C is shown for $Tb_5Si_2Ge_2$, giving $\frac{dT_S}{dH_C} \sim 2.3$ K/T, whereas for the $Gd_5Si_2Ge_2$ compound, the value found was $\frac{dT_S}{dH_C} \sim 7.1$ K/T (see supplementary material[18]), which is similar to the predicted value.[6] Including the obtained $T_C^{O(I)}$ in the *(x, T)* magneto-structural phase diagram for the $Tb_5(Si_xGe_{1-x})_4$ system, one notices that this value is in agreement with the those expected from the linear extrapolation of temperature (Fig. 2(c)) of the Si-rich *O(I)* region. This observation is also in accordance with the Gd case.[6] This fact strengthens the idea that the formation of the covalent Si(Ge)-Si(Ge) bonds in the interlayer region indeed increases the exchange interaction, in accordance with previous experimental and theoretical measurements.[15] From the obtained results, it can be stressed that both *O(I)* and *M* phases exhibit a 2nd-order (continuous) PM to FM transition (see continuous Brillouin curves in Fig. 2(a)). Consequently, the 1st order magnetostructural transition experimentally observed is always a consequence of the change of the crystallographic structure. In fact, the M→O(I) transition is always discontinuous since the symmetry group of the *O(I)* phase is not a sub-group of the *M* one.[16] Considering a simple thermodynamic model for $Tb_5Si_2Ge_2$ compound, the total free energy (*F*) per ion (at constant volume) for a crystalline system at temperature *T* and under H (Ref. 6) is given by

$$F(T,\sigma) = U_{lat} - HgJ\sigma - \frac{3}{2}\frac{J}{J+1}k_B T_C \sigma^2 - TS_M - TS_{lat}, \quad (1)$$

where σ is the reduced magnetization, the first term U_{lat} is the non-magnetic internal energy, the second term is the Zeeman term, the third one is the magnetic ion-ion exchange interaction energy, and the last two terms are the entropy contributions (magnetic and lattice, respectively). Using *ab-initio* calculation (local spin-density approximation method), one obtains 0.11 eV for F_M-$F_{O(I)}$ at T = 0 K which is equal to the energy difference between the U_{lat} of both structures. The magnetic entropy per ion (S_M) can be estimated by the following approximation,[6] excluding the fourth-order parameter, $O(\sigma^4)$:

$$S_M(\sigma) \sim k_B\left[ln(2J+1) - \frac{3}{2}\frac{J}{J+1}\sigma^2 + O(\sigma^4)\right]. \quad (2)$$

The magnetic equation of state ($\sigma(T, H)$) can be obtained by finding the zero of the derivative of Eq. (1) with respect to σ [leading to $\sigma = \sigma(T, H)$], which corresponds to the condition of the free energy minimum. This free energy minimum is then given by $F^{min}(T, H) = F[T, \sigma(T, H)]$. For the lattice entropy term, one can rely on the Debye approximation where the entropy per ion is given by the following approximated expression:[12]

$$S_{lat}(T) \sim 4k_B - 3k_B ln\left(\frac{\Theta_D}{T}\right) + \frac{3}{40}k_B\left(\frac{\Theta_D}{T}\right)^2 + O\left[\left(\frac{\Theta_D}{T}\right)^3\right], \quad (3)$$

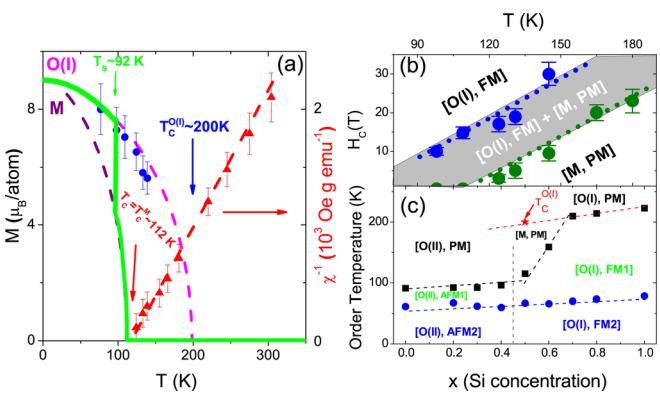

FIG. 2. (Color online) (a) Temperature dependence of the spontaneous magnetization (blue dots) and reciprocal susceptibility (red triangle) curves of $Tb_5Si_2Ge_2$ obtained from Arrot representation. The dashed lines (dash lines) are the spontaneous magnetization Brillouin curves assuming $T_C^M = 112$ K and $T_C^{O(I)} = 200$ K. (b) Temperature dependence of the $H_C(T)$. (c) Magnetic and crystallographic phases diagram of $Tb_5(Si_xGe_{1-x})_4$ taken from Ref. 8 including the determined value of $T_C^{O(I)}$ (star). The square represents the temperature of the order-disorder transition (for x > 0.45: PM → FM and for x < 0.45 from PM to AFM state). The circle symbols represent the order-order transition also called spin reorientation transition.

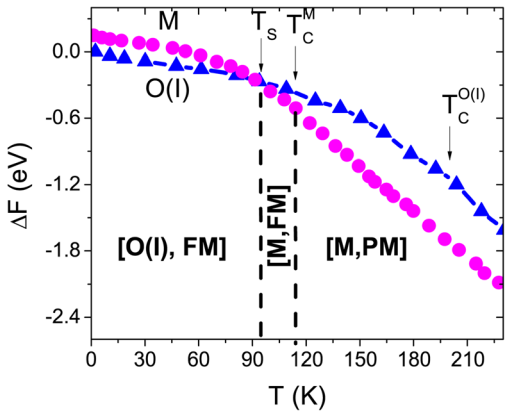

FIG. 3. (Color online) Change in the magnetic free energy as a function of temperature of both structures (*M* and *O(I)*) for $Tb_5Si_2Ge_2$ using Eq. (1).

where Θ_D is the (cut-off) Debye temperature. Using the value of $\Theta_D^{O(I)} \sim 170\,\mathrm{K}$ from Ref. 17 and the relation $\frac{\Theta_D^M}{\Theta_D^{O(I)}} = 1 - \eta\frac{\Delta V}{V}$, where η is the Grüneisen parameter ($\eta \sim 10$ for $Gd_5Si_2Ge_2$)[12] and $\frac{\Delta V}{V}$ is around $\sim$1%, one can estimate the Θ_D^M to be $\sim$153 K. Considering both Θ_D's and Eq. (3), the S_{lat} contribution for the total free energy in $Tb_5Si_2Ge_2$ is found to be smaller than 10% of the total free energy. This result has similar magnitude as the one previously obtained by Liu *et al.*[12] for Gd case showing that the main contribution arises from the magnetic entropy variation. Concerning all contributions for the $F(T, \sigma)$ per ion (Fig. 3) [$[\Delta F_{O(I)}^{min}]$ and $[\Delta F_M^{min}]$] in the $Tb_5Si_2Ge_2$ material, a crossover of the free energies is noticed at $T_S = 92.2$ K, meaning that our model predicts a structural transition at this particular temperature. In fact, this result is in accordance with the experimental data ($T_S = 95$ K; on cooling). As can be inferred from Eq. (1), the effect of a magnetic field is to the decrease of the free energy. However, due to the different T_C's of each crystal structure, the free energy of the crystallographic phase with higher $T_C^{O(I)}$ suffers a higher decrease than the one with lower T_C^M, thus increasing the $T_S(H)$, where $F_M(\mathrm{H}) = F_{O(I)}$ (H), and explaining the observed linear dependence in $H_C(T)$ (see Fig. 2(b)) and the Gd compound case. As a first glance, these results can be important scenarios for the analysis of the occurrence of (de)coupling of MST on the $R_5(Si_xGe_{1-x})_4$ system: i.e., in the case of $T_C^M < T_S < T_C^{O(I)}$ (under cooling), the system changes simultaneously its magnetic and crystallographic phases through a [*M*, PM]→[*O(I)*, FM] 1st-order transition. This situation occurs in $Gd_5Si_2Ge_2$ reported in Ref. 6. In the case of $T_S < T_C^M < T_C^{O(I)}$, the system first exhibits (under cooling) a magnetic second order phase transition at $T_C^M[(M, \mathrm{PM}) \rightarrow (M, \mathrm{FM})]$ and some degrees below, at T_S, changes its crystallographic structure through a [*M*, FM]→[*O(I)*, FM] 1st-order phase transition. In this situation, one says that the magnetic and structural transitions are decoupled, and this is what occurs in the $Tb_5Si_2Ge_2$ compound. In summary, one shows that the variation of the magnetic energy of each phase is the main contribution to the free energy and is sufficient to induce a first-order structural transition when two crystallographic structures present different T_C's. Furthermore, from high magnetic field experiments and Arrott plot construction, we were able to determine experimentally the (different) T_C's of each structure. Concerning the technological applications on MR, we stress that the ideal MCE material should present a strong competition between two crystallographic structures with two distinct critical temperatures. The variation of the magnetic entropy energy will be maximized when the crossover of the free energies (marking the occurrence of the structural transition) occurs exactly at the temperature of the lowest T_C. Nevertheless, it should be highlighted that these types of transitions usually exhibit magnetic hysteresis which is a drawback for the technological applications. The development of materials with distinct critical temperatures and without hysteresis losses constitutes the major challenge on the near future. We believe that our findings discussed herein will open new avenues on the search for this tournament, thus leading to the production of optimal magnetic materials exhibiting giant MCE.

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[1]K. A. Gschneidner, Jr. and V. K. Pecharsky, Annu. Rev. Mater. Sci. **30**, 387 (2000).
[2]K. A. Gschneidner, Jr., V. K. Pecharsky, and A. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[3]V. Pecharsky and K. Gschneidner, Jr., Adv. Mat. **13**, 683 (2001).
[4]L. Morellon, P. A. Algarabel, M. R. Ibarra, J. Blasco, B. Garcia-Landa, Z. Arnold, and F. Albertini, Phys. Rev. B **58**, R14721 (1998).
[5]C. Magen, L. Morellon, P. A. Algarabel, M. R. Ibarra, Z. Arnold, J. Kamarad, T. A. Lograsso, D. Schlagel, V. K. Pecharsky, A. O. Tsokol, and K. A. Gschneidner, Jr., Phys. Rev. B **72**, 024416 (2005).
[6]D. Paudyal, V. K. Pecharsky, K. A. Gschneidner, Jr., and B. N. Harmon, Phys. Rev. B **73**, 144406 (2006).
[7]V. K. Pecharsky, K. A. Gschneidner, Jr., Ya. Mudryk, and D. Paudyal, J. Magn. Magn. Mater. **321**, 3541 (2009).
[8]L. Morellon, J. Blasco, P. A. Algarabel, and M. R. Ibarra, Phys. Rev. B **62**, 1022 (2000).
[9]L. Morellon, C. Ritter, C. Magen, P. A. Algarabel, and M. R. Ibarra, Phys. Rev. B **68**, 024417 (2003).
[10]V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[11]A. M. Pereira, A. M. Santos, C. Magen, J. B. Sousa, P. A. Algarabel, Y. Ren, C. Ritter, L. Morellon, M. R. Ibarra, and J. P. Araujo, Appl. Phys. Lett. **98**, 122501 (2011).
[12]G. J. Liu, J. R. Sun, J. Lin, Y. W. Xie, T. Y. Zhao, H. W. Zhang, and B. G. Shen, Appl. Phys. Lett. **88**, 212505 (2006).
[13]P. Blaha, K. Schwarz, G. K. H. Madsen, and J. L. Kvasnicka, Wien2K—An augmented plane wave + local orbitals program for calculating crystal properties, available at www.wien2k.at (2011).
[14]A. Arrott, Phys. Rev. **108**, 1394 (1957).
[15]D. Haskel, Y. B. Lee, B. N. Harmon, Z. Islam, J. C. Lang, G. Srajer, Y. Mudryk, K. A. Gschneidner, and V. K. Pecharsky, Phys. Rev. Lett. **98**, 247205 (2007).
[16]N. Bocarra, *Symtries Brisées* (Herman, Paris, 1976).
[17]M. B. Gomes and N. A. de Oliveira, J. Magn. Magn. Mater. **320**, 153 (2009).
[18]See supplementary material at http://dx.doi.org/10.1063/1.3640213 for where it is briefly described the Arrott analysis as well as the complementary results on $Gd_5Si_2Ge_2$ compound.